

ATTACHMENT B

UREA-FORMALDEHYDE ADHESIVE RESINS*

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Approximately 1 million metric tons of urea-formaldehyde resin are produced annually. More than 70% of this urea-formaldehyde resin is used by the forest products in-

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dustry for a variety of purposes.¹ The resin is used in the production of an adhesive for bonding particleboard (61% of the urea-formaldehyde used by the industry), medium-density fiberboard (27%), hardwood plywood (5%), and a laminating adhesive for bonding (7%), for example, furniture case goods, overlays to panels, and interior flush doors.

Urea-formaldehyde resins are the most prominent examples of the class of thermosetting resins usually referred to as amino resins.^{2,3} Urea-formaldehyde resins comprise about 80% of the amino resins produced worldwide. Melamine-formaldehyde resins constitute the remainder of this class of resins, except for minor amounts of resins that are produced from other aldehydes or amino compounds (especially aniline), or both.

Amino resins are often used to modify the properties of other materials.^{2,3} These resins are added during the processing of such products as textile fabrics to impart permanent press characteristics; automobile tires to improve the bonding of rubber to tire cord; paper to improve the tear strength, especially of wet paper; and alkyds and acrylics to improve their cure. Amino resins are also used for molding products, such as electrical devices, jar caps, buttons, and dinnerware, and in the production of countertops.

The use of urea-formaldehyde resins as a major adhesive by the forest products industry is due to a number of advantages, including low cost, ease of use under a wide variety of curing conditions, low cure temperatures, water solubility, resistance to microorganisms and to abrasion, hardness, excellent thermal properties, and lack of color, especially of the cured resin.

The major disadvantage associated with urea-formaldehyde adhesives as compared with other thermosetting wood adhesives, such as phenol-formaldehyde and polymeric diisocyanates, is the lack of resistance to moist

conditions, especially in combination with heat. These conditions lead to a reversal of the bond-forming reactions and the release of formaldehyde. For this reason, urea-formaldehyde resins are usually used for the manufacture of products intended for interior use only. However, even when used for interior purposes, the slow release of formaldehyde (a suspected carcinogen) from products bonded with urea-formaldehyde adhesives is a major concern that has come under close scrutiny by state and Federal regulatory agencies.

CHEMISTRY OF UREA-FORMALDEHYDE RESIN FORMATION

Urea-formaldehyde resins are formed by the reaction of urea and formaldehyde. The overall reaction of urea with formaldehyde is quite complex and, although initially studied early in this century, is not completely understood at the present time.⁴

The synthesis of a urea-formaldehyde resin takes place in two stages. In the first stage, urea is hydroxymethylolated by the addition of formaldehyde to the amino groups (Figure 1). This reaction is in reality a series of reactions that lead to the formation of mono-, di-, and trimethylolureas. Tetramethylolurea is apparently not produced, at least not in a detectable quantity.

The addition of formaldehyde to urea takes place over the entire pH range (Figure 2). The reaction rate is dependent on the pH. The rate for the addition of formaldehyde to successively form one, two, and three methylol groups has been estimated to be in the ratio of 9:3:1, respectively.⁴ The exact ratio, of course, is dependent on the reaction conditions employed in the addition reaction.

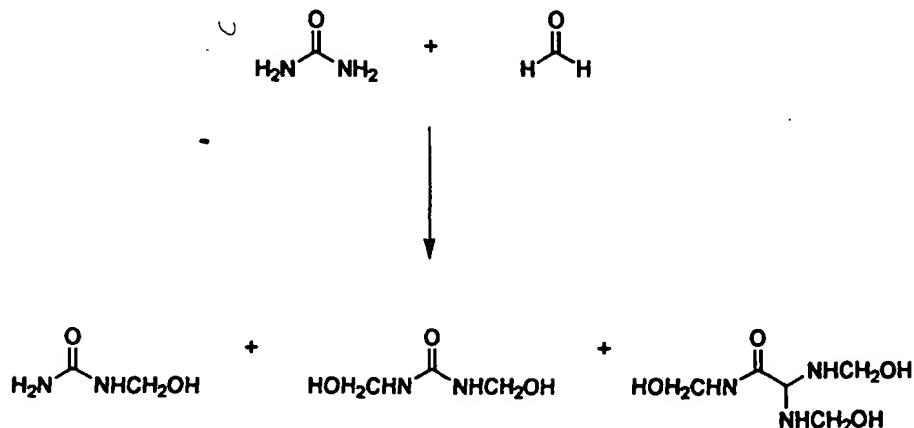


FIGURE 1. Formation of mono-, di-, and trimethylolurea by the addition of formaldehyde to urea. Tetramethylolurea has not been observed experimentally.

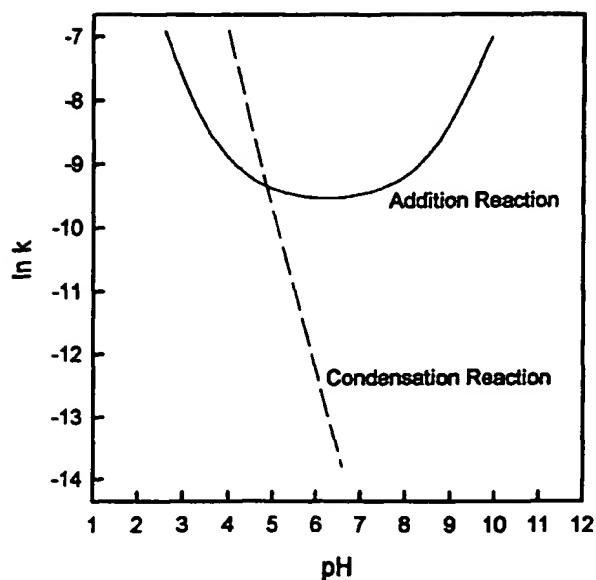


FIGURE 2. Influence of pH on the rate constant (k) for addition and condensation reactions of urea and formaldehyde. *Source:* Adapted from Reference 10. With permission.

The second stage of urea-formaldehyde resin synthesis consists of the condensation of the methylolureas to low molecular weight polymers. The rate at which these condensation reactions occur is very dependent on the pH (Figure 2) and, for all practical purposes, occurs only at acidic pHs. The increase in the molecular weight of the urea-formaldehyde resin under acidic conditions is thought to be a combination of reactions leading to the formation of:

- methylene bridges between amino nitrogens by the reaction of methylol and amino groups on reacting molecules (Figure 3a);
- methylene ether linkages by the reaction of two methylol groups (Figure 3b);
- methylene linkages from methylene ether linkages by the splitting out of formaldehyde (Figure 3c); and
- methylene linkages by the reaction of methylol groups splitting out water and formaldehyde in the process (Figure 3d).

The difference between the pH profiles of the two stages of urea-formaldehyde resin synthesis is used to advantage in the production of urea-formaldehyde adhesive resins. In general, the commercial production of urea-formaldehyde

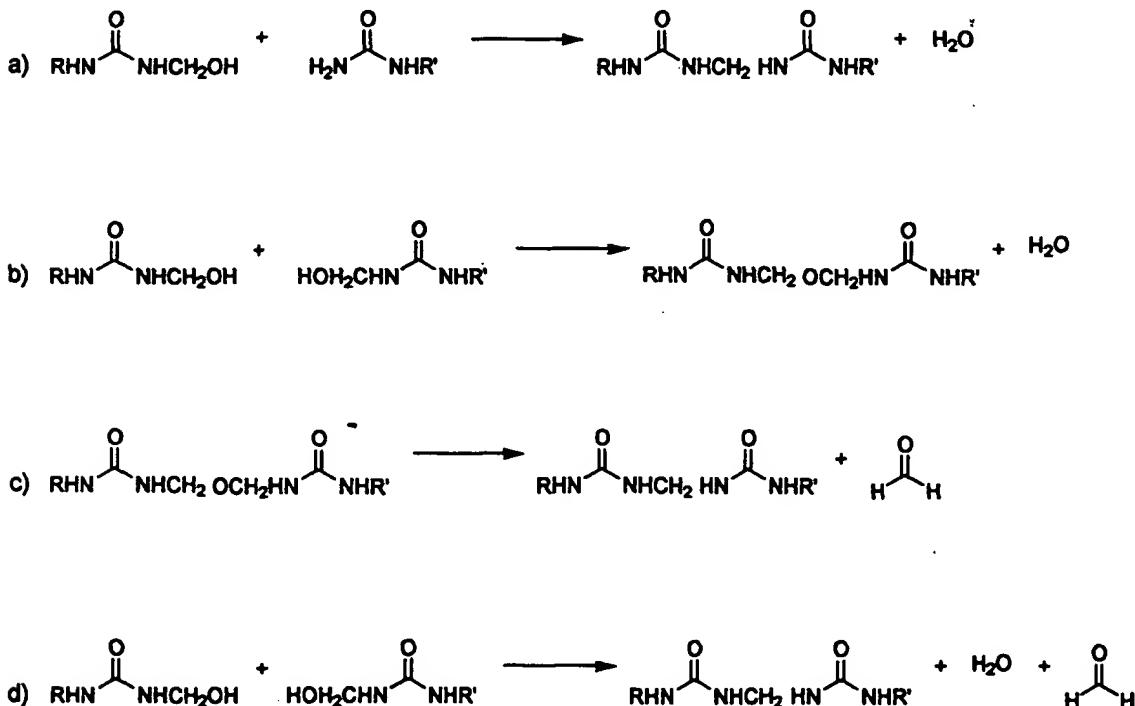


FIGURE 3. Condensation reactions of methylolureas to form (a) methylene bridges between amino nitrogens, (b) methylene ether linkages, and (c) and (d) methylene linkages. Reactions of these types produce higher molecular weight oligomers and polymers.

adhesive resins is carried out in two major steps. The first step consists of the formation of methylolureas by the reaction of urea and formaldehyde under basic conditions with a pH of ~8-9. This step is carried out under basic conditions to allow the methylation reactions to proceed in the absence of reactions involving the condensation of the methylolureas.

In the second step, the reaction mixture is brought to the acid side, with a pH of about 5, and the condensation reactions are carried out until a desired viscosity is reached. Then, the reaction mixture is cooled and neutralized. Water is removed by vacuum distillation to give a resin with a desired solids content (typically about 60-65%). Urea is often added in two, or sometimes more, steps. The initial addition of urea is made during the methylation step, in which the formaldehyde-to-urea (F/U) ratio is typically large (~ 1.6-2). Usually, the second addition of urea is made during the condensation step. The second and any subsequent additions of urea lower the final F/U ratio to the desired level.

These procedures for the synthesis of urea-formaldehyde adhesive resins offer a wide range of conditions which make possible the synthesis of resins with important properties such as tack, gel time, and spreadability for the uncured resin. Formaldehyde emissions and the durability of the cured resin can be controlled and specifically tailored for the final end use of the resin.

An acidic-cure catalyst is added to the urea-formaldehyde resin before it is used as an adhesive. Ammonium chloride and ammonium sulfate are the most widely used catalysts for resins used by the forest products industry. A variety of other acids can be used as a catalyst, including formic acid, boric acid, phosphoric acid, oxalic acid, and acid salts of hexamethylenetetramine.

Resin cure is normally conducted at a temperature of ~120 °C and a pH < 5. The reactions that occur during the final cure of the resin are thought to be similar to those that occur during the acid condensation of the methylolureas. The traditional viewpoint is that these reactions lead to the formation of a crosslinked polymeric network for the hardened, cured resin. However, there is evidence that a colloidal phase also occurs during resin cure.⁵⁻⁷ This evidence illustrates the lack of a full understanding of the physical and chemical processes leading to the cure of urea-formaldehyde resin systems and the need for continued research.

FORMALDEHYDE EMISSION FROM UREA-FORMALDEHYDE RESINS

Few issues in the forest products industry rival the debate and concern over the emission of formaldehyde from products bonded with urea-formaldehyde adhesive resins.

This issue originated in the mid-1970s as the increasing use of formaldehyde-emitting panel products in the more tightly constructed homes led to numerous complaints. This has resulted in an increasing scrutiny of formaldehyde emission levels from building products used within homes by state and national regulatory agencies, including the Housing and Urban Development (HUD) and the Environmental Protection Agency (EPA), and the adoption by industry of voluntary standards for the emission of formaldehyde from wood products bonded with urea-formaldehyde adhesive resin, most notably particleboard. Similar concerns in Europe led to the well-known E-1 standard limiting formaldehyde emissions from particleboard used in construction. In response to consumer concerns and regulatory actions, the particleboard, medium-density fiberboard, and hardwood plywood industries have made major strides in reducing formaldehyde emission levels from products bonded with urea-formaldehyde adhesive resins (Figure 4).

The evolution of formaldehyde from urea-formaldehyde materials is incontrovertible. Over the past 40 years, investigators have examined extensively the structure of components of urea-formaldehyde resin systems and the physical chemistry of their formation and degradation in aqueous solutions. Classical kinetic, chromatographic, and NMR techniques have been applied.⁸⁻²⁸ We can conclude from these studies that the reactions leading to the formation of the urea-formaldehyde products formed during urea-formalde-

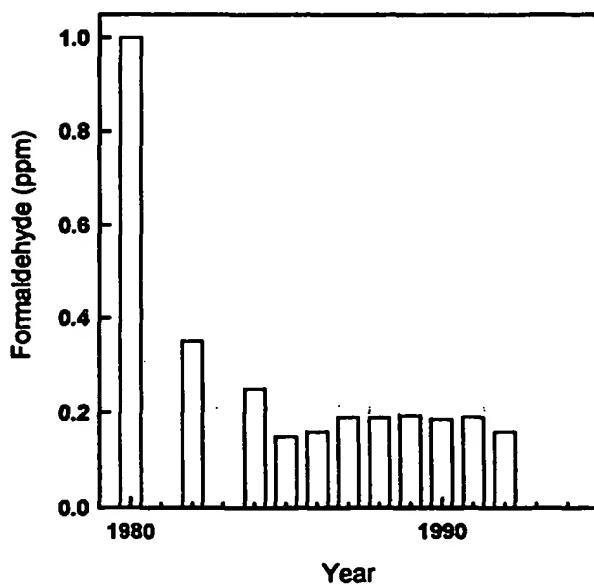


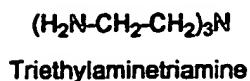
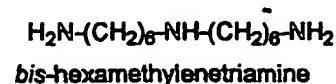
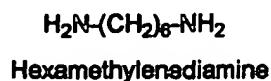
FIGURE 4. Average formaldehyde emission levels from particleboard manufactured in the year indicated. The levels were determined by the large chamber test method. Source: National Particleboard Association.

hyde resin synthesis and cure are reversible. In the forward direction, water is eliminated; therefore, the reverse reactions can be viewed as hydrolysis, which leads to the release of formaldehyde.²⁹ Because most, if not all, of these reactions are catalyzed by acid, the use of an acid catalyst to hasten bond cure unfortunately also increases the rate of hydrolysis and formaldehyde liberation.

The reduction in formaldehyde emission levels from products bonded with urea-formaldehyde adhesive resins has been achieved by employing one or more of several technological methods.³⁰ In general, these methods include:

- changing the formulation of the urea-formaldehyde adhesive resin (e.g., lowering the F/U ratio);
- adding formaldehyde-scavenging materials directly to the urea-formaldehyde adhesive resin;
- separately adding formaldehyde-scavenging materials to the wood finish,
- treating panels after their manufacture either with a formaldehyde scavenger or by the application of coatings or laminates; and
- changing to an entirely different adhesive resin system.

The most widely used approach for reducing formaldehyde emission levels has emphasized decreasing the mole ratio of F/U. Ratios of about 1.6 that were common 10 to 15 years ago have now been reduced to values as low as 1.0 and, in some cases, lower. Unfortunately, lowering the F/U ratio produces resins with less tolerance for processing variations and panels that often have poorer physical and structural properties³¹ As a consequence, some panel manufacturers use adhesive resins with a higher F/U ratio and employ other methods to achieve the necessary reduction in formaldehyde emission levels.



Recent research has suggested possible new methods to lower formaldehyde emission levels. This research involves two strategies: the modification of the chemistry of urea-formaldehyde resins and the replacement of the formaldehyde component in urea-formaldehyde resins with a less volatile aldehyde or its chemical equivalent.

Research involving the first strategy sought to chemically modify urea-formaldehyde resins with polyamines (Figure 5), primarily to improve durability and stability by decreasing the internal stresses developed during resin cure and increase the ability of the cured resin to withstand cyclic stresses.³²⁻³⁷

Urea-formaldehyde resins were modified by:

- incorporating the polyamines directly during resin synthesis;
- incorporating the polyamines in the form of urea-capped derivatives during resin synthesis;
- using the polyamine hydrochloride salts as cure catalysts in place of ammonium chloride; and
- using a combination of the last two methods.

The direct addition of the free amines during resin cure produced uncurable resins. In general, modification with urea-capped amines or curing with amine hydrochlorides provided cure rates comparable with that of unmodified urea-formaldehyde resins cured with ammonium chloride. These modifications also reduced the tendency of the resin to crack and fracture and substantially improved the resistance of bonded joints to the stress imposed by cyclic wet-dry exposures. Resins cured with the amine hydrochlorides had less formaldehyde liberation than those cured with ammonium chloride. These results indicate that the incorporation of flexible polyamines offers promise for improv-

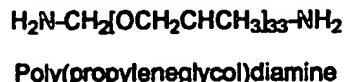
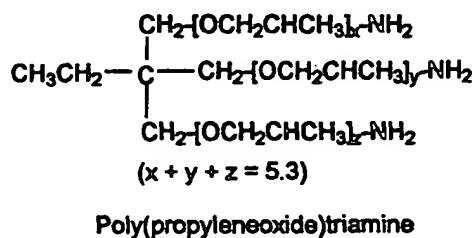


FIGURE 5. Structures of di- and triamines used to modify urea-formaldehyde resins to increase the stability and durability of the cured adhesive resin.

ing the durability and stability of urea-formaldehyde-bonded wood products and possibly for reducing formaldehyde emissions.

Research involving the second strategy, that is, the substitution of reactive components for formaldehyde in urea-formaldehyde resins, is presently in progress. The formaldehyde substitutes that have been tried to date have not been fully successful in replacing formaldehyde, presumably as a result of the lower reactivity of these substitutes with urea and urea-formaldehyde resins. However, the use of at least one alternative aldehyde in the formulation of a urea-formaldehyde-type resin has been patented.³⁸

Both strategies show promise and indicate that further research along both lines of investigation should be pursued.

CONCLUSION

Urea-formaldehyde resin is a major commercial adhesive, especially within the forest products industry. It offers a number of advantages when compared with other adhesive systems. However, despite the fact that great strides have been made to offset its major disadvantage by lowering the formaldehyde emission levels of products bonded with urea-formaldehyde adhesive resin, the industry still faces the possibility of more restrictive regulations on formaldehyde in dwellings. Moreover, tighter restrictions on formaldehyde levels in the workplace are also likely. New research efforts are needed to address this concern if urea-formaldehyde adhesive resins are to maintain their prominent position as a versatile adhesive system.

REFERENCES

- White, J. T. *For. Prod. J.* 1995, 45(3), 21.
- Williams, L. L. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Kroschwitz, J. I.; Howe-Grant, M. Eds.; John Wiley & Sons: New York, NY; 1991; Vol. 2, pp 604–637.
- Updegraff, I. H. In *Handbook of Adhesives*, 3rd ed.; Skeist, I., Ed.; van Nostrand Reinhold: New York, 1990; 341–346.
- Pizzi, A. In *Wood Adhesives: Chemistry and Technology*; Pizzi, A., Ed.; Marcel Dekker: New York, 1983.
- Pratt, T. J.; Johns, W. E.; Rammon, R. M.; Plagemann, W. L. *J. Adhesion* 1985, 17, 275.
- Stuligross, J.; Koutsky, J. A. *J. Adhesion* 1995, 18, 281.
- Motter, W. K. Ph.D. Thesis, Washington State University, 1990.
- de Jong, J. I.; de Jonge, J. *Rec. Trav. Chim.* 1952, 71, 643.
- de Jong, J. I.; de Jonge, J. *Rec. Trav. Chim.* 1952, 71, 661.
- de Jong, J. I.; de Jonge, J. *Rec. Trav. Chim.* 1953, 72, 139–156.
- Landquist, N. *Acta Chem. Scand.* 1955, 9, 1466.
- Landquist, N. *Acta Chem. Scand.* 1955, 9, 1471.
- Dunn, A. S. *J. Chem. Soc.* 1957; 1446.
- Symthe, L. E. *J. Amer. Chem. Soc.* 1953, 75, 1508.
- Price, A. F.; Cooper, A. R.; Meskin, A. S. *J. Appl. Polym. Sci.* 1980, 25, 1611.
- Kumar, A.; Sood, A. *J. Appl. Polym. Sci.* 1990, 40, 1473.
- Kumlin, K.; Simonson, R. *Angew. Makromol. Chem.* 1978, 68, 175.
- Katuscak, S.; Thomas, M.; Sciessl, O. *J. Appl. Polym. Sci.* 1981, 26, 381.
- Dunky, M.; Lederer, K. *Angew. Makromol. Chem.* 1982, 102, 199.
- Ludlam, P. R.; King, J. G. *J. Appl. Polym. Sci.* 1984, 29, 3863.
- Slonim, I. I.; Alekseeva, S. G.; Urman, I. G.; Arshava, B. M.; Akselrod, B. I. *Vysokomol. Soed.* 1978, 29(7), 1477.
- Tomita, B. In *C-13 NMR Analysis of urea-formaldehyde Resins, Tech. Workshop on Formaldehyde*, Vol. II, Consumer Product Safety Commission, National Bureau of Standards: Gaithersburg, MD, 1980.
- Nair, B. R.; Francis, D. *J. Polymer* 1983, 24, 626.
- Ebdon, J. R.; Heaton, P. E.; Huckerby, T. N.; O'Rourke, W. T. S.; Parkin, J. *Polymer* 1984, 25, 821.
- Chuang, I.-S.; Hawkins, B. L.; Maciel, G. E.; Myers, G. E. *Macromols.* 1985, 18(7), 1482.
- Kim, M. G.; Amos, L. W. *Ind. Eng. Chem. Res.* 1990, 29, 208.
- Pizzi, A.; Lipschitz, L.; Valenzuela, J. *Holzforschung* 1994, 48(3), 254.
- Chuang, I.-S.; Maciel, G. E. *J. Appl. Polym. Sci.* 1994, 52, 1637.
- Myers, G. E. In *Wood Adhesives in 1985: Status and Needs*; Christiansen, A. W. et al., Eds.; Forest Prod. Res. Soc.: Madison, WI, 1986.
- Myers, G. E. Advances in Methods to Reduce Formaldehyde Emission, In *Composite Board Products for Furniture and Cabinets—Innovations in Manufacture and Utilization*; Hamel, M. P., Ed.; Forest Prod. Soc.: Madison, WI, 1989.
- Myers, G. E. *For. Prod. J.* 1984, 34(5), 35.
- Ebewele, R. O.; Myers, G. E.; River, B. H.; Koutsky, J. A. *J. Appl. Polym. Sci.* 1991, 42, 2997.
- Ebewele, R. O.; River, B. H.; Myers, G. E.; Koutsky, J. A. *J. Appl. Polym. Sci.* 1991, 43, 1483.
- Ebewele, R. O.; River, B. H.; Myers, G. E. *J. Appl. Polym. Sci.* 1993, 49, 229.
- Ebewele, R. O.; River, B. H.; Myers, G. E. *Adhes. Age* 1993, 36(13), 23.
- Ebewele, R. O.; River, B. H.; Myers, G. E. *J. Appl. Polym. Sci.* 1994, 52, 689.
- River, B. H.; Ebewele, R. O.; Myers, G. E. *Holz als Roh- und Werkstoff* 1994, 52, 179.
- Detlefsen, W. D.; Wen-I-Shiau, D.; Daisy, N. K. U.S. Patent 5 059 488, 1991.